Applied Surface Science
Room 324/325 - Session AS-WeM
High-K Materials Interface Analysis

Moderator: H.G. Tompkins, Consultant

8:20am **AS-WeM1 Spectroscopic Characterization of High-k Dielectrics: Applications to Interface Electronic Structure and Stability Against Chemical Phase Separation***, G. Lucovsky, **Cristiano Krug**,* North Carolina State University **INVITED**

The lowest conduction band states of high-k transition metal and rare earth dielectrics are associated with localized anti-bonding d*-states. Combining X-ray absorption spectroscopy, XAS, with vacuum ultra-violet spectroscopic ellipsometry, VUV SE, photoconductivity, PC, and internal photoemission, IPE, provides a way to study final state effects, in particular different d*-states, and d*-s*-state splittings which can then be compared with ab initio calculations on small clusters. These studies prove important insights into empirical correlations between i) band gaps, and ii) conduction band offset energies with respect to crystalline silicon and atomic d-state energies which apply to both transition metal and rare earth dielectrics, including binary oxides, and silicate and aluminate alloys. These results provide important insights into optimization of silicate and aluminate alloys for minimum direct tunneling at a given equivalent oxide capacitance. Combining Fourier transform infra red spectroscopy, FTIR, and derivative X-ray photoelectron spectroscopy, XPS, with extended X-ray absoroption fine structure spectroscopy, EXAFS, provides an unambiguous way to differentiate between chemical phase separation with different degrees of crystallization in Zr and Hf silicate gate dielectrics, and at their interfaces with Si. This is of importance for semiconductor device processing since chemical phase separation at 900C (1000C) in silicon dioxide-rich Zr (Hf) silicates not detectable by X-ray diffraction, XRD, reduces gate dielectric capacitance, and therefore can reduce current drive in field effect transistors, FETs.

9:00am **AS-WeM3 Effect of Nitrogen on Interface Stability of Plasma Enhanced Chemical Vapor Deposition of Hafnium Oxide on Si(100)***, **P. Chen**, H. Bhandari, T.M. Klein,* The University of Alabama

Hafnium oxide is a potential high dielectric constant material for use in field effect transistor gate applications. Interface quality, especially for chemical vapor deposited films, is a concern, however, and is the motivation for the introduction of nitrogen. Plasma enhanced chemical vapor deposition (PECVD) was used to grow hafnium oxide thin films on Si using Hf tert-butoxide and N@sub 2@O or N@sub 2@ remote plasma. Upto 6 at.% N was obtained using a N@sub 2@/He plasma. Angle resolved x-ray photoelectron spectroscopy indicates the nitrogen is located at the oxide/Si interface. Stability of the interface is enhanced with nitrogen treatment showing a smaller increase in film thickness after annealing in argon.

9:20am **AS-WeM4 High-k Al@sub 2@O@sub 3@-HfO@sub 2@ Layers for CMOS Applications Studied by XPS and ToF-SIMS***, **R.G. Vitchev**, L. Houssiau, J.J. Pireaux,* Facultes Universitaires Notre-Dame de la Paix, Belgium

High-k metallic oxides are considered as promising candidates to replace SiO@sub2@ as a gate dielectric in the future CMOS devices. Al@sub 2@O@sub 3@-HfO@sub 2@ mixed oxide layers deposited by Atomic Layer Chemical Vapor Deposition on differently pretreated silicon wafers (0.5 nm and 1 nm SiO@sub 2@ grown by rapid thermal oxidation as well as HF-last Si surface) were characterized by single- and two emission angle XPS and by ToF-SIMS dual beam depth profiling (250 eV Xe@super +@ and Cs@super +@ sputtering beam, 15 keV Ga@super +@ analysis beam). The composition and the depth distribution of constituent elements were measured for mixed oxide layers deposited with different number of cycles (and hence with different thickness) and different Hf/Al cycle ratios. It was found that the Hf/Al content ratio for the thinnest films was much higher than for the thicker films with the same cycle ratio. The surface region of the thicker films was enriched in Al (and depleted in Hf) indicating a preferential deposition of HfO@sub 2@ at the film/silicon interface. The depth distribution of impurities was also measured and compared. The interfacial SiO@sub 2@ layer thickness was determined as well as the oxidation state of Si atoms in it. Changes of the interfacial SiO@sub 2@ layer thickness and chemistry after prolonged air exposure were followed. Work performed under EU-CUHKO project.

9:40am **AS-WeM5 Materials Characterization and Processing Effects on Hafnium-based Gate Dielectrics***, **W.R. Nieveen**,* Charles Evans & Associates/Evans Analytical Group*; P.S. Lysaght,* International SEMATECH*; G. Goodman, I. Mowat, B. Schueler,* Charles Evans & Associates/Evans Analytical Group*; J.A. Bennett, B. Foran, M. Gardner, R.W. Murto, H.R. Huff,* International SEMATECH

Introduction of high-k gate dielectrics into semiconductor processing is proving to be a formidable challenge due to the electrical performance requirements and insufficient understanding of the variations in physical characteristics as a function of thermal processing. Relevant device parameters including gate leakage current density, EOT, V@sub t@ instabilities, V@sub fb@ shift, and electron and hole mobility are affected by process conditions that alter the materials properties. Such physical parameters include phase orientation, oxygen coordination, onset temperature of crystallization, etc. Optimization of process parameters, which affect the material properties and lead to improved device performance with good integration properties, is todays challenge in high-k materials. In this work, we focus on advanced material characterization of various hafnium-silicon-oxygen composition systems and correlate the physical data with specific aspects of transistor performance. A comprehensive and complimentary set of Hf silicate samples, exposed to an incremental range of thermal process treatments, are characterized by XPS, HRTEM, HAADF, EELS, conductive AFM, and SIMS. Fundamental issues associated with phase separation in Hf-Si-O (and HfSiON) systems are discussed within the context of relevant capacitor and transistor device performance. We will discuss the correlation of physical material parameters measured by various analytical techniques with process conditions, and electrical parameters and measurements.

10:00am **AS-WeM6 Synchrotron UPS and EXAFS Analysis of High-k and Si Interfaces***, **Y.-S. Lin**, R. Puthenkovilakam, J.P. Chang,* University of California, Los Angeles

Ultra-thin dielectric films with high permittivity such as ZrO@sub 2@, HfO@sub 2@, and HfO@sub x@N@sub y@ have numerous applications in advanced microelectronics, especially on silicon substrates for gate dielectric application in metal-oxide-semiconductor (MOS) devices. In this work, we combine synchrotron based ultra-violet electron spectroscopy (UPS) and extended x-ray absorption fine structures (EXAFS) analysis to characterize the interface of ZrO@sub 2@, HfO@sub 2@, and HfO@sub x@N@sub y@ on silicon. Specifically, the interfacial composition and chemical coordination of the deposited metal oxides and oxynitrides films on silicon are determined. By tuning the photon energy in UPS analysis, we determined the composition of the interfaces between high-k dielectrics and silicon and their corresponding valence band structures. The experimental results were compared to first principle calculations using density functional theory to validate the measurements and elucidate the effect of chemical coordination at the interface on the electronic structure, band gap, and band offsets. The energy shifts measured in oxygen s and p states compared favorably with first principle calculations and closely related to the bonding to metal atoms. The Fourier transformed EXAFS spectra also agreed very well with the first principle prediction and allowed the determination of interatomic spacings and the chemical nature of the nearest and second-nearest neighboring atoms. Based on the experimental validation, we used density functional theory to calculate the electronic band gaps, conduction and valence band offsets, and interface states for dielectric/Si interfaces, and found that these properties are greatly affected by the metal, oxygen, and nitrogen coordinations.

10:20am **AS-WeM7 Determination of ToF Medium Energy Backscattering Capabilities for Interfacial Analysis***, **R.D. Geil**, B.R. Rogers, D.W. Crunkleton, Z. Song, R.A. Weller,* Vanderbilt University

Time-of-flight medium energy backscattering (ToF-MEBS) is a unique surface analysis technique developed at Vanderbilt initially for determining levels of transition metal contaminants on silicon surfaces. The technique's high sensitivity and depth resolution makes it highly suitable for the analysis of ultra-thin films, such as gate dielectrics. The interface between the gate dielectric and silicon is of particular interest because it is a dominant factor in determining the overall electrical properties of the gate structure.@footnote 1@ In order to determine the extent of information about the lower interface region of a gate dielectric that ToF-MEBS can provide, we have studied a well-characterized material system, SiO@sub 2@/Si. Thermally grown SiO@sub 2@ films with thicknesses ranging from 2-10 nm were analyzed to determine how interfacial information degrades with depth into the sample. Thickness and stoichiometric information at the bulk and interfacial regions were determined. Channeling in the direction of the Si substrate was performed to suppress background. TEM analysis was performed on the films to confirm ToF-MEBS thickness values. Spectroscopic ellipsometry was also used for thickness comparisons. XPS analysis provided extra interfacial and compositional information. @FootnoteText@ @footnote 1@ Wilk, G.D., R.M. Wallace, and J.M. Anthony, High-K Gate Dielectrics: Current Status and Materials Properties Considerations. Applied Physics Review, 2001. 89(10): p. 5243-5275.

10:40am **AS-WeM8 Investigation of PECVD TiO@sub 2@ on Silicon***, **P.R. McCurdy**, L. Sturgess, S. Kohli, E.R. Fisher,* Colorado State University

Continuous wave (CW) and equivalently powered, pulsed radio frequency plasmas were used to deposit thin films of titanium dioxide on to Si(100) substrates. In these experiments oxygen plasmas were created by feeding oxygen gas through the coil region, titanium (IV) isopropoxide was introduced downstream from the plasma region. These films have been characterized using XRD, XPS, SEM and AES. XRD showed that TiO2 films deposited at substrate temperatures Â³350ÂºC are polycrystalline with an anatase structure, while at lower substrate temperatures the films were amorphous. Results show high quality films were produced with some carbon incorporation. Annealing these films in vacuum at 900 oC show the TiO2/Si interfacial region to be reduced to Ti2O3, while Si is oxidized to SiOx. Upon annealing at a 950oC further reduction of the TiO2 film was noted to include TiO. The 950oC film partially re-oxided upon exposure to atmosphere. XRD of annealed films showed no crystalline structure of these annealed films. SEM of the TiO2 film surfaces showed the as deposited films were smooth and structureless and remained so even when annealed at 850oC. Annealing at 950oC caused the surface to become very rough, resulting in the rupturing of the TiO2 surface thus exposing areas of the underlying Si/SiO2 substrate.

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